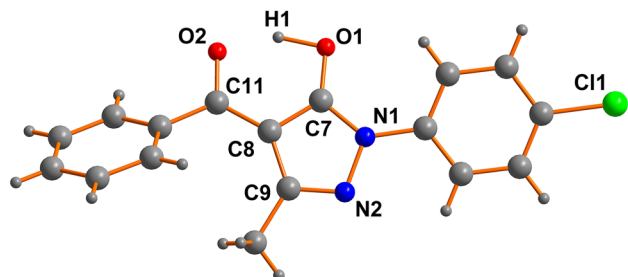


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Crystal structure of 1-(4-chlorophenyl)-4-benzoyl-3-methyl-1*H*-pyrazol-5-ol, C₁₇H₁₃ClN₂O₂



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Abstract

C₁₇H₁₃ClN₂O₂, monoclinic, *P*₂/*c* (no. 14), *a* = 5.3601(4) Å, *b* = 10.6233(7) Å, *c* = 25.2125(16) Å, β = 92.920(5)°, *V* = 1433.96(17) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0495, *wR*_{ref}(*F*²) = 0.1143, *T* = 173(10) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

All reagents were obtained from commercial sources and used without further purification. 1-(4-chlorophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one was synthesized according to the method proposed by Jensen (1959) (yield 84.5 %; m.p. 441–443 K). 1-(4-chlorophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (5 g) was dissolved in dioxane (100 mL) by warming and Ca(OH)₂ (3 g), added. Benzoyl chloride (5 mL) was next added, drop by drop, with stirring within 3 min. After

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.21 × 0.20 × 0.18 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.28 mm ^{−1}
Diffractometer, scan mode:	Xcalibur
θ _{max} , completeness:	26.0°, >99 %
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	9041, 2823, 0.034
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2101
<i>N</i> (<i>param</i>) _{refined} :	205
Programs:	CrysAlis ^{Pro} [1], SHELX [2, 3], WinGX/ORTEP [4], PLATON [5]

refluxing gently for 1 h, the orange mixture was cooled and poured with stirring into chilled 3 M HCl (300 mL). A handful of ice-salt mixture was added and vigorous stirring continued for another 30 min, after which, the reaction mixture was kept in a refrigerator until crystallization occurred. Filtration of the product gave 85 % yield of light yellow crystals.

2 Experimental details

The hydroxyl H atom was located in a difference Fourier map. Other H atoms were placed in calculated positions, with C—H = 0.93 for phenyl and furan, and refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C) for phenyl H.

3 Comment

Acylpyrazolones are an interesting class of β-diketones, containing a pyrazole-bearing chelating arm [6]. Thus, they can coordinate with a variety of metal elements to generate complexes with different structures [7, 8]. A few years ago, we have synthesized heterocyclic acylpyrazolone ligands substituted by chlorine at the position 1 and studied their crystal structures [9, 10]. In order to expand this field, we use the methyl and benzoyl substituents at the 3- and 4-positions in the formation of the title compounds.

The structure of the title compound is shown in the Figure. Atom O1 shows the lengthening of the C7=O1 bond [1.296(3) Å] relative to that normally found for carbonyl groups and this atom acts as hydrogen-bond acceptor. The

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
H1	0.056 (7)	−0.066 (3)	0.6030 (15)	0.122 (17)*
C1	−0.1608 (4)	0.2371 (2)	0.53180 (9)	0.0265 (5)
C2	−0.3509 (6)	0.1569 (3)	0.51696 (12)	0.0521(9)
H2	−0.364144	0.079411	0.533765	0.063*
C3	−0.5247 (6)	0.1911 (3)	0.47674 (13)	0.0586 (10)
H3	−0.655149	0.136858	0.466881	0.070*
C4	−0.5038 (5)	0.3038 (3)	0.45182 (9)	0.0322 (6)
C5	−0.3212 (6)	0.3846 (3)	0.46711 (14)	0.0686 (11)
H5	−0.311048	0.462877	0.450872	0.082*
C6	−0.1479 (6)	0.3504 (3)	0.50728 (15)	0.0736 (12)
H6	−0.020760	0.406141	0.517587	0.088*
C7	0.0763 (4)	0.0917 (2)	0.59513 (9)	0.0275 (5)
C8	0.2767 (4)	0.1102 (2)	0.63315 (9)	0.0260 (5)
C9	0.3365 (4)	0.2416 (2)	0.62861 (9)	0.0270 (5)
C10	0.5451 (5)	0.3167 (2)	0.65451 (10)	0.0322 (6)
H10A	0.569739	0.391991	0.634369	0.048*
H10B	0.695557	0.267581	0.655844	0.048*
H10C	0.503730	0.338772	0.689922	0.048*
C11	0.3756 (4)	0.0040 (2)	0.66088 (9)	0.0274 (5)
C12	0.5677 (4)	0.0102 (2)	0.70553 (9)	0.0253 (5)
C13	0.7527 (4)	−0.0819 (2)	0.70921 (9)	0.0295 (6)
H13	0.756870	−0.144696	0.683580	0.035*
C14	0.9304 (5)	−0.0800 (3)	0.75096 (10)	0.0355 (6)
H14	1.055730	−0.140560	0.753035	0.043*
C15	0.9216 (5)	0.0120 (3)	0.78959 (10)	0.0364 (6)
H15	1.041651	0.013079	0.817550	0.044*
C16	0.7355 (5)	0.1025 (2)	0.78697 (9)	0.0346 (6)
H16	0.728746	0.163350	0.813372	0.042*
C17	0.5587 (5)	0.1019 (2)	0.74466 (9)	0.0290 (6)
H17	0.434339	0.163016	0.742540	0.035*
Cl1	−0.72236 (14)	0.34509 (7)	0.40096 (3)	0.0487 (2)
N1	0.0205 (4)	0.20465 (19)	0.57295 (7)	0.0273 (5)
N2	0.1853 (4)	0.29791 (19)	0.59323(8)	0.0300 (5)
O1	−0.0338 (3)	−0.01341 (16)	0.58243 (7)	0.0356 (5)
O2	0.2955 (3)	−0.10533 (16)	0.64727 (6)	0.0345 (4)

intermolecular O—H...O hydrogen bond results in the formation of a dimer with an R²₂(12) graph-set motif [12]. It is apparent that the C11=O2 and C8=C11 distances correspond to well defined double bonds. The conjugation effects also cause the pyrazolone and C1–C6 benzene ring to be nearly coplanar, with a mean deviation from the overall plane of 0.010 Å. Atoms O1, C7, C8, C11 and O2 are essentially coplanar, the largest deviation from the mean plane being 0.044 Å for C11. The dihedral angle between the C1–C6 benzene ring and the pyrazolone ring is 18.56(2)°. The clear presence of the hydroxyl H atom in the difference Fourier synthesis and the absence of any residual electronic density in the vicinity of O1 confirm that the title compound crystallizes as a pure hydroxyl tautomer and that no

desmotropism is present [13]. All bond lengths and angles are normal and comparable with those found for related compounds [11, 14, 15].

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